$\lambda_2 = e^{-ika}$ and the corresponding functions are $\psi_1(x)$ and $\psi_2(x)$. The functions have the property

$$\psi_1(x+a) = e^{ika}\,\psi_1(x),$$

and $$\psi_2(x+a) = e^{-ika}\,\psi_2(x). \qquad \ldots(19)$$

Such functions are called Bloch functions. The functions are written in the form

$$\psi(x) = e^{\pm ikx}\,u_k(x)$$

and have the property

$$\begin{aligned}\psi(x+a) &= e^{\pm ik(x+a)}\,u_k(x+a),\\ &= e^{\pm ikx}\,e^{\pm ika}\,u_k(x),\\ &= e^{\pm ika}\,\psi(x),\end{aligned}$$

which has the same general form as equation (19). Thus the solution of Schroedinger wave equation in this region can be expressed in the form of Bloch function $\psi(x) = e^{\pm ikx}\,u_k(x)$, where $u_k(x) = u_k\,(x+a)$.

(2) *For energy range in which* $(\alpha_1+\beta_2)^2 > 4$.

In this case the two roots are real. The solutions of the Schroedinger equation are of the type.

$$\psi_1(x) = u^{\mu x}\,u(x) \text{ and } \psi_2(x) = e^{-\mu x}\,u(x).$$

where μ is a real quantity. These solutions are mathematically sound but they can not be accepted as the wavefunctions. Thus there are no electronic states in this region corresponding to real roots λ_1 and λ_2.

The conclusion of the above discussion is that the energy spectrum of an electron in a periodic potential consists of allowed and forbidden energy regions or bands. The complex values of μ correspond to allowed energy bands, while real values of μ correspond to forbidden energy bands. The details are considered in the next article as suggested by Kronig and Penney.

9.4. THE KRONIG-PENNEY MODEL :

One of the simplest examples of one dimensional periodic potential has been treated by Kronig and Penney. It is assumed

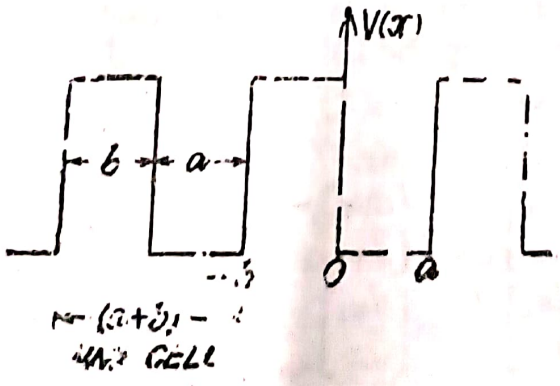

Fig. 6 (a). Showing a periodic array of square wells.

that the potential energy of an electron has the form of a periodic array of square wells, as shown in figure 6 (a) and it is possible to obtain an exact solution of Schroedinger equation. The period of the potential is $(a+b)$; in regions such as $0 < x < a$ the potential energy is assumed equal to zero; in the regions such as $-b < x < 0$ the potential energy is V_0.

Although it is somewhat idealized periodic potential and is only approximation to be found in actual crystal but it illustrates many important features of the quantum behaviour of electron in periodic lattice.

The Schroedinger wave equations for two regions are

$$\frac{d^2\psi_1}{dx^2}+\frac{2m}{\hbar^2}E\psi_1=0 \quad \text{for} \quad 0 < x < a, \qquad \ldots(1)$$

and

$$\frac{d^2\psi_2}{dx^2}+\frac{2m}{\hbar^2}[E-V_0]\,\psi_2=0 \quad \text{for} \quad -b < x < 0 \qquad \ldots(2)$$

Here it is assumed that the energy E of the electron is smaller than V_0. Again let

$$\frac{2mE}{\hbar^2}=\alpha^2 \quad \text{and} \quad \frac{2m(V_0-E)}{\hbar^2}=\beta^2, \qquad \ldots(3)$$

where α and β are two quantities.

Now the wave functions must be Bloch form, hence

$$\psi(x)=e^{ikx}\,u_k(x).$$

Substituting equation (3) in equation (1) and (2) we get

$$\frac{d^2u_1}{dx^2}+2ik\frac{du_1}{dx}+(\alpha^2-k^2)\,u_1=0 \qquad 0 < x < a \qquad \ldots(4)$$

and

$$\frac{d^2u_2}{dx^2}+2ik\frac{du_2}{dx}-(\beta^2+k^2)\,u_2=0 \qquad -b < x < 0, \qquad \ldots(5)$$

where $u_1(x)$ represents the value of $u_k(x)$ in the interval $(0<x<a)$ and $u_2(x)$ represents the value of $u_k(x)$ in the interval $(-b<x<0)$.

The solutions of equations (4) and (5) are

$$u_1(x)=Ae^{i(\alpha-k)x}+Be^{-i(\alpha+k)x} \qquad 0 < x < a, \qquad \ldots(6)$$

and

$$u_2(x)=Ce^{(\beta-ik)x}+De^{-(\beta+ik)x} \qquad -b < x < 0, \qquad \ldots(7)$$

where A, B, C and D are constants. The value of these constants can be obtained by applying the following conditions

$$\begin{aligned}
&[u_1(x)]_{x=0}=[u_2(x)]_{x=0},\\
&[u_1(x)]_{x=a}=[u_2(x)]_{x=-b},\\
&\left[\frac{du_1}{dx}\right]_{x=0}=\left[\frac{du_2}{dx}\right]_{x=0}\\
&\left[\frac{du_1}{dx}\right]_{x=a}=\left[\frac{du_2}{dx}\right]_{x=-b}
\end{aligned} \qquad \ldots(8)$$

Applying these conditions, we have

$$A+B=C+D, \qquad \ldots(9)$$

$$i(\alpha-k)A-i(\alpha+k)B=(\beta-ik)C-(\beta+ik)D, \quad \ldots(10)$$

$$Ae^{i(\alpha-k)a}+Be^{-i(\alpha+k)a}=Ce^{-(\beta-ik)b}+De^{(\beta+ik)b}, \quad \ldots(11)$$

and $i(\alpha-k)Ae^{i(\alpha-k)a}-i(\alpha+k)e^{-i(\alpha+k)a}=(\beta-ik)Ce^{-(\beta-ik)b}$

$$-(\beta+ik)\times De^{(\beta+ik)b} \quad \ldots(12)$$

The equations 9, 10, 11 and 12 have a solution only if the determinant of the coefficients A, B, C and D vanish, *i.e.*,

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha-k) & -i(\alpha+k) & (\beta-ik) & -(\beta+ik) \\ e^{i(\alpha-k)a} & e^{-i(\alpha+k)a} & e^{-(\beta-ik)b} & e^{(\beta+ik)b} \\ i(\alpha-k)e^{i(\alpha-k)a} & -i(\alpha+k)e^{-i(\alpha+k)a} & (\beta-ik)e^{-(\beta-ik)b} & -(\beta+ik)e^{(\beta+ik)b} \end{vmatrix}=0 \quad \ldots(13)$$

Solving the determinant we have

$$\frac{\beta^2-\alpha^2}{2\alpha\beta}\sinh\beta b\sin\alpha a+\cosh\beta b\cos\alpha a=\cos k(a+b). \quad \ldots(14)$$

In order to consider a more convenient equation, Kronig and Penney considered the case when V_0 tends to infinity and b approaches zero, but the product V_0b remains finite, *i.e.*, the case in which the potential barrier becomes delta function. Equation (14) then reduces to

$$\frac{mV_0k}{\hbar^2\alpha}\sin\alpha a+\cos\alpha a=\cos ka \quad \ldots(15)$$

because $b\to 0$, $\sinh\beta b\to\beta b$

and $\cosh\beta b\to 1$

$$\therefore \quad P\frac{\sin\alpha a}{\alpha a}+\cos\alpha a=\cos ka. \quad \ldots(16)$$

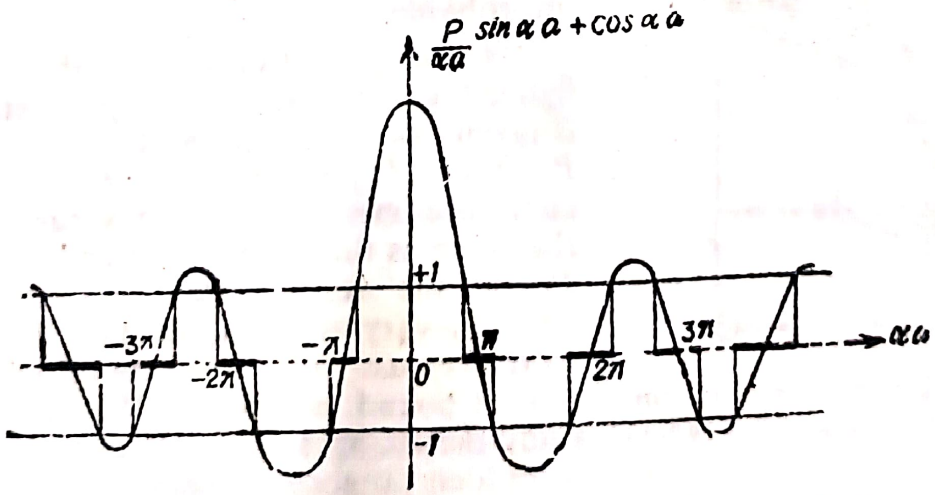

Fig. 6 (b). The plot of L.H.S. of equation (16) as a function of αa for $P=3\pi/2$. The allowed regions are heavily drawn.

The left hand side of equation (16) is plotted as a function of αa for the value of $P=3\pi/2$. The right hand side can take only

values between -1 to $+1$ as indicated by the horizontal lines in figure 6(b). Therefore, the condition (16) can be satisfied only for values of αa for which left hand side lies between ± 1.

From the figure following conclusions are drawn :

(1) The energy spectrum of electrons consists of a number of allowed energy bands separated by forbidden bands.

(2) The width of allowed energy band increases with increasing energy values, *i.e.*, with the increasing values of αa. This is due to the fact that the first term of equation (16) decreases on the average with increasing αa.

(3) With increasing P, *i.e.*, with increasing binding energy of the electrons, the width of a particular allowed band decreases. For $P \to \infty$ the allowed energy region becomes infinitely narrow and the energy spectrum is a line spectrum. The equation (16) has only solution of $\sin \alpha a = 0$.

i.e., $$\alpha a = \pm n\pi,$$

or $$\alpha = \pm \frac{n\pi}{a}, \text{ or } \alpha^2 = \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}.$$

or $$E = \frac{n^2\pi^2\hbar^2}{2ma^2}. \qquad \ldots(17)$$

This expression shows that the energy is dependent on k. This equation shows the energy levels of a particle in a constant potential box of atomic dimensions. This is expected because for large P tunneling through the barrier becomes improbable.

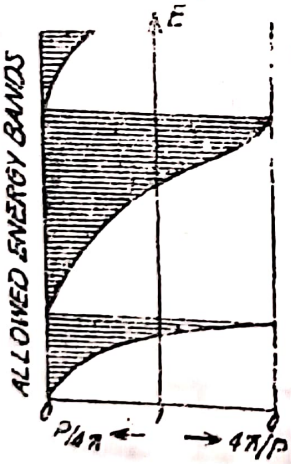

Fig. 6(c). Allowed and forbidden energy ranges (shaded and open respectively) as function of P. The extreme left corresponds to $P=0$ (free electrons) and extreme right to $P=\infty$.

These conclusions are shown in figure 6(c), where the energy spectrum is given as a function of P. When $P=0$, *i.e.*; V_0 is zero, the E versus P curve becomes a continuous parabola, the same as that of a free electron. For $P \to \infty$ the result is a line spectrum. Thus by varying the quantity P from 0 to ∞ we pass from the case of free to that of bound electrons. We can also study the changes in the allowed and forbidden ranges of energy as the wave functions.

(4) Using equations (16) it is possible to plot a curve showing the energy E as a function of k. This result is shown in figure 7.

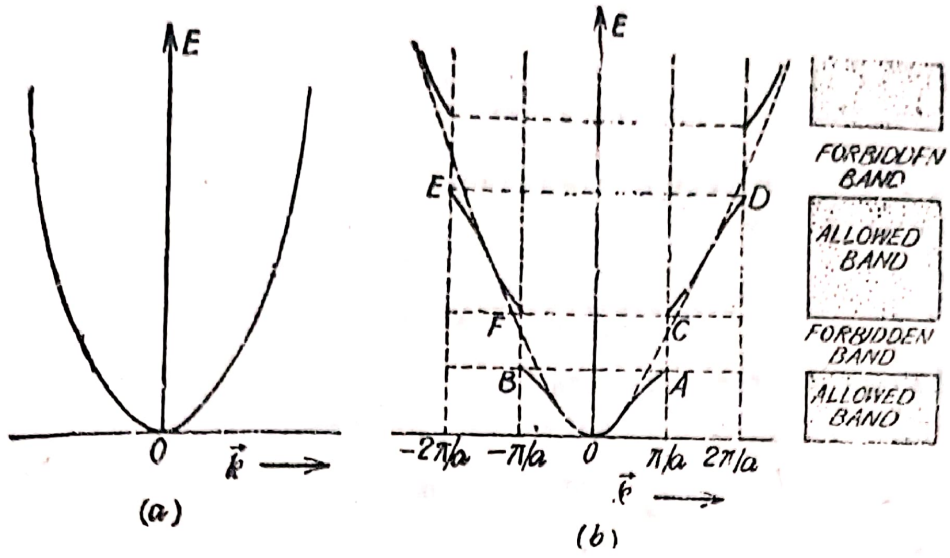

Fig. 7. Showing allowed and forbidden bands.

The discontinuities in the E versus k curve occurs for

$$k=\frac{n\pi}{a}, \text{ where } n=\pm 1, \pm 2, \pm 3,.....$$

This shows that the energy of the electron increases continuously from zero unit the value of k reaches π/a. The electron thus meets a wall and gets reflected. We know that when X-ray is incident normal to a set of planes of spacing a, it suffers reflection according to the condition

$$n\lambda=2a \sin 90, \quad \text{or} \quad n\lambda=2a.$$

Substituting $k=n\pi/a$ and equating it to $2\pi/\lambda$, we obtain the condition of Bragg reflection. Now considering the electrons as waves and propagation of electrons through the crystal analogous to the propagation of electromagnetic waves, and using $n\lambda=2a$, we find that electron suffers Bragg reflection when $n=\pm 1$, ± 2, ± 3 corresponding to I, II and III order reflections, and so on.

The range of allowed values of k between $-\pi/a$ and $+\pi/a$ constitutes the first Brillouin zone. Similarly, the second one consists of two parts; One extending from π/a to $2\pi/a$ and another part between $-\pi/a$ and $-2\pi/a$. These zero boundaries represent the maximum energies that the electron can have without developing any discontinuity. The energy gap at the zone boundary is called the forbidden zone and the electron travelling along the length of linear lattice in the above case can not have these energies.

Velocity of the electron in periodic potential field : According to de-Broglie idea, an electron moving with velocity v is considered as a wave packet moving with the group velocity v_g, which is equal